

Form PTO-1390
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U.S. DEPARTMENT OF COMMERCE
PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

P21954

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

10/031932

INTERNATIONAL APPLICATION NO.

PCT/EP00/06768

INTERNATIONAL FILING DATE

15 July 2000

PRIORITY DATE CLAIMED

27 July 1999

TITLE OF INVENTION

LITHIUM OXIDE-CONTAINING LITHIUM INTERCALATION COMPOUNDS

APPLICANT(S) FOR DO/EO/US

Günter HEIL, Claudius KORMANN, and Jörg ADEL

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

1. ☒ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to promptly begin national examination procedures (35 U.S.C. 371(f)).
4. ☒ The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371 (c)(2)).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3))
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
"Unexecuted"
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (U.S.C. 371(c)(5)).

Items 11 to 16 below concern other document(s) or information included:

11. Assignee: EMTEC MAGNETICS GMBH of Ludwigshafen, GERMANY _____
12. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
13. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
14. ☒ A FIRST preliminary amendment.
☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☒ Figure of Drawing to be published _____
18. ☒ Other items or information:
Cover Sheet and International Application as published in German.
PCT/IPEA/416(in German).
PCT/IPEA/409(in German).
PCT/ISA/210(in German and English).
Cover Letter under 35 U.S.C. 371 and 1.495.
Claim of Priority.

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

10/031932

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19. ☒ The following fees are submitted:

Basic National Fee (37 CFR 1.492(a)(1)-(5)):

Search report has been prepared by the EPO or JPO. \$ 890.00

International preliminary examination fee paid to USPTO (37 CFR 1.482). \$ 710.00

No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)). \$ 740.00

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO. \$1,040.00

International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4). \$ 100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

CALCULATIONS

PTO USE ONLY

\$890.00

Surcharge of \$130.00 for furnishing the oath or declaration later than 20 30 months from the earliest claimed priority date (37 CFR 1.492(e)).

\$

Claims

Number Filed

Number Extra

RATE

Total Claims

26 - 20 =

6

X \$18.00

\$108.00

Independent Claims

1 - 3 =

0

X \$84.00

\$0.00

Multiple dependent claim(s) (if applicable)

+ \$280.00

\$

TOTAL OF ABOVE CALCULATIONS =

\$998.00

☐ Applicant claims small entity status See 37 CFR 1.27. The fees indicated above are reduced by $\frac{1}{2}$.

\$

SUBTOTAL =

\$998.00

Processing fee of \$130.00 for furnishing the English translation later than 20 30 months from the earliest claimed priority date (37 CFR 1.492(f))

+

Extension of Time fee in the amount of \$

TOTAL NATIONAL FEE =

\$998.00

Fee for recording the enclosed assignment (37 CFR 1.21(h). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property

+

TOTAL FEES ENCLOSED =

\$998.00

Amount to be refunded

\$

Charged

\$

a. ☒ A check in the amount of \$998.00 to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. in the amount of \$ to cover the above fees.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 19-0089.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO CUSTOMER NO. 7055
AT THE PRESENT ADDRESS OF:

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PATENT TRADEMARK OFFICE

SIGNATURE
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NAME

28,394
REGISTRATION NUMBER

P21954.A02

#3/a

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Gunter HEIL et al.

Group Art Unit: Unknown

Appl. No. : Not Yet Assigned (National Stage of PCT/EP00/06768)

Examiner: Unknown

I.A. Filed : July 15, 2000

For : LITHIUM OXIDE CONTAINING
LITHIUM INTERCALATION COMPOUNDS

PRELIMINARY AMENDMENT

Assistant Commissioner of Patents
Washington, D.C. 20231

Sir:

Prior to calculation of the filing fees and examination of the above-identified patent application, entry of the following amendment is respectfully requested.

IN THE CLAIMS

Please amend claims 4, 5, 6, 8, 12, 14, 15, 16 and 18, as follows (a marked-up copy of the changes is attached in an Appendix to the present amendment):

4. (Amended) A lithium oxide-containing lithium intercalation compound as claimed in claim 1, where the agglomerate size, determined from the d_{50} value, is greater than 10 μm .

5. (Amended) A lithium oxide-containing lithium intercalation compound as claimed in claim 1, where the diameter, determined from the d_{90} value, is smaller than 50 μm .

6. (Amended) A lithium oxide-containing lithium intercalation compound as claimed in claim 1, where the diameter, determined from the d_{90} value, is smaller than 40 μm .

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8. (Amended) A lithium oxide-containing lithium intercalation compound as claimed in claim 2, where lithium manganese oxide is present.

12. (Amended) A process as claimed in claim 10, where the suspending in water is carried out with addition of polyvinyl alcohol as binder.

14. (Amended) A process as claimed in claim 10, where the heating in an oxidizing atmosphere is carried out in a rotary tube furnace at a temperature of from 725°C to 900°C and a residence time of from 0.5 to 6 hours.

15. (Amended) A process as claimed in claim 10, where the heating in an oxidizing atmosphere is carried out in a stationary furnace at a temperature of from 600°C to 750°C and a residence time of greater than 5 hours.

16. (Amended) A process as claimed in claim 10, where, after the heating in an oxidizing atmosphere, the resultant solid is suspended in water with addition of one or more alkaline lithium compounds, and the suspension is spray-dried at a temperature of from 100°C to 400°C.

18. (Amended) A process as claimed in claim 9, where the intimate mixing and/or the suspension is carried out with addition of a binder in the presence of a sintering aid with a concentration of from 0.1 to 3%, based on the weight of the solids employed.

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**APPENDIX
MARKED-UP COPY OF CHANGES TO CLAIMS**

4. (Amended) A lithium oxide-containing lithium intercalation compound as claimed in [claims 1 to 3] claim 1, where the agglomerate size, determined from the d_{50} value, is greater than $10\ \mu\text{m}$.

5. (Amended) A lithium oxide-containing lithium intercalation compound as claimed in [claims 1 to 4] claim 1, where the diameter, determined from the d_{90} value, is smaller than $50\ \mu\text{m}$.

6. (Amended) A lithium oxide-containing lithium intercalation compound as claimed in [claims 1 to 4] claim 1, where the diameter, determined from the d_{90} value, is smaller than $40\ \mu\text{m}$.

8. (Amended) A lithium oxide-containing lithium intercalation compound as claimed in [claims 2 to 6] claim 2, where lithium manganese oxide is present.

12. (Amended) A process as claimed in [claim 10 or 11] claim 10, where the suspending in water is carried out with addition of polyvinyl alcohol as binder.

14. (Amended) A process as claimed in [any of claims 10 to 13] claim 10, where the heating in an oxidizing atmosphere is carried out in a rotary tube furnace at a temperature of from 725°C to 900°C and a residence time of from 0.5 to 6 hours.

15. (Amended) A process as claimed in [any of claims 10 to 13] claim 10, where the heating in an oxidizing atmosphere is carried out in a stationary furnace at a temperature of from 600°C to 750°C and a residence time of greater than 5 hours.

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16. (Amended) A process as claimed in [any of claims 10 to 13 and 14 or 15] claim 10, where, after the heating in an oxidizing atmosphere, the resultant solid is suspended in water with addition of one or more alkaline lithium compounds, and the suspension is spray-dried at a temperature of from 100°C to 400°C.

18. (Amended) A process as claimed in [any of claims 9 to 17] claim 9, where the intimate mixing and/or the suspension is carried out with addition of a binder in the presence of a sintering aid with a concentration of from 0.1 to 3%, based on the weight of the solids employed.

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Lithium oxide-containing lithium intercalation compounds

Description

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The present invention relates to improved lithium oxide-containing lithium intercalation compounds for thin-film electrodes, to a process for their preparation, to electrodes produced therefrom, and to secondary lithium ion batteries containing lithium oxide-containing lithium intercalation compounds as active material of the positive electrode.

Lithium batteries can be made from one or more electrochemical cells which contain electrochemically active pigments. Cells of this type typically consist of an anode (negative electrode), a separator, a cathode (positive electrode) and an electrolyte. Batteries containing metallic lithium as anode are known, as are those containing graphite, coke or other carbon particles which, as is known, are able to intercalate alkali metal ions. Also known are batteries containing other lithium intercalation compounds, i.e. substances which are able to incorporate and release lithium under the action of an electric potential. The electrolyte typically consists of a lithium salt dissolved in one or more aprotic, normally organic solvents. Further suitable electrolytes are solid electrolytes which consist of a polymeric matrix containing an ionically conductive, but electronically insulating medium. The charging process is generally defined in such a way that the anode (the negative pole) takes up lithium ions during charging, while the cathode (the positive pole) serves as a source of lithium ions. Cells containing lithium metal as anode are usually charged during assembly.

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Cells with anodes containing graphite or other carbon or another host substance which is capable of taking up lithium ions are usually uncharged during assembly. In order that they can be used as energy stores, they must
5 be connected and charged against an intercalation compound containing lithium ions, preferably an intercalation compound containing lithium oxide. During charging, the lithium ions migrate from the intercalation compound to the graphite or carbon or
10 another host substance which is capable of taking up lithium ions. The cell can then be discharged again, during which the lithium moves back. Rechargeable batteries of this type which do not contain metallic lithium are known as lithium ion batteries. Examples
15 thereof are described in US 4,464,447 and US 5,418,090.

LiCoO_2 , LiMn_2O_4 and LiNiO_2 are preferably employed as oxidic materials in the cathodes. All these compounds are also employed with varied mixing ratios of the
20 metal ions in order to establish certain advantages in charging or in the service life. Some or all of the oxygen is sometimes replaced by other elements, for example fluorine or sulfur. While the cobalt compounds are expensive, the nickel compounds are difficult to
25 prepare. By contrast, manganese compounds are relatively cheap.

The specific charge of LiMn_2O_4 is theoretically 148 milliampere hours per gram. This value can be changed
30 by varying the oxygen content or the ratio between the lithium and the manganese. In the opinion of many experts, however, LiMn_2O_4 can only reversibly cycle about 110-120 milliampere hours per gram, corresponding to about 0.8 mol of lithium per formula unit, in the
35 long term. In the case of LiNiO_2 and LiCoO_2 , only about 0.5 mol of lithium per formula unit can be reversibly cycled. The situation is more favorable in the case of

mixed nickel oxides, in which some of the nickel has been replaced by cobalt or another metal, metalloid or transition metal. Mention may be made by way of Example of $\text{Li}_1\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$. The use of integer coefficients 1 for lithium or 2 for oxygen serves only to simplify the formula description; in practice, fractional values are also used due to intentional or unintentional variation of the amounts of starting materials. Experience teaches that the elements can be varied in broad – not only even numbered – mixing ratios, giving intercalation compounds which are suitable for use in cathodes. It is essential that the compounds contain lithium ions and elements that are sufficiently capable of changing their electric charge.

In the meantime, many processes for the preparation of intercalation compounds for use in cathodes have been described. Thus, the preparation of LiNO_2 by high-temperature synthesis has already been described in J. Amer. Chem. Soc. 76, 1499 (1954). US 4,302,518 describes the synthesis of $\text{Li}_x\text{Co}_y\text{O}_2$ by heating a mixture of lithium carbonate and cobalt carbonate at 900°C in air, followed by two further heating steps. This specification also describes the synthesis of $\text{Li}_x\text{Ni}_y\text{O}$ by heating $\text{LiOH} \cdot x \text{H}_2\text{O}$ and nickel powder under oxygen at 750°C with subsequent grinding and further heating steps. US 4,507,371 teaches that lithium intercalation compounds having the cubic ion lattice $(\text{B}_2)\text{X}_4^{n-}$ can be synthesized by various reactions: solid-state reactions from the pulverulent elements or compounds thereof at high temperatures, ion exchange methods or chemical or electrochemical titration techniques. US 4,980,080 describes a process for the preparation of $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ which comprises the following steps: 1) preparation of a mixture of powders, 2) heating the mixture in air at $600\text{--}800^\circ\text{C}$, 3) optionally: homogenization of the heated product and repetition of the powder heating.

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A wet-chemical process for the preparation of a lithium manganese oxide spinel is described in DE 19 515 629. Here, a lithium compound and a manganese salt are reacted in the disperse phase and dried, after which
5 the dry residue is subjected to a sequence of grinding and heating steps. A further wet-chemical synthetic process is described in US 5,742,070. It is essentially based on the preparation of solutions of lithium, transition metal and organic acids and alcohols, which
10 are subsequently dried, ground and heated.

PCT application WO 97/37935 claims a dry preparation process in which mixtures of manganese oxides and lithium compounds, each with a controlled particle size
15 distribution, are repeatedly heated at selected temperatures. PCT application WO 98/02931 describes a process for the preparation of lithium manganese intercalation oxides which consists of the reaction of LiOH, MnO₂ and at least one polyfunctional alcohol
20 followed by heat treatment.

While the known preparation processes led to certain improvements in the properties of lithium intercalation oxides, they do not satisfy the high demands made by
25 the use of such substances in electrodes, in particular cathodes of lithium ion batteries. In particular, there has hitherto been no success in preparing lithium intercalation compounds which, on use, have both high specific charges and high loadability of the batteries
30 produced therewith. A further disadvantage of the prior art is that many highly specialized processes exist for the preparation of lithium intercalation compounds which do not allow variations in the composition and at the same time in the morphology and of the crystal
35 structure of the compounds produced.

It is an object of the present invention to provide lithium intercalation compounds of high specific charge which, depending on the application, are able to supply a high power density or a high energy density in batteries produced therewith and ensure high loadability of these batteries. It is a further object of the invention to provide a simple process for the preparation of lithium intercalation compounds of this type with which specific influencing with respect to a high power density or high energy density of the batteries produced therefrom is possible and which can be applied to a different elemental composition of the lithium intercalation compounds and to different morphologies. It is a further object of the invention to provide electrodes which, on use in batteries, achieve high loadability, high specific charge and high power density or high energy density of these batteries. It is a further object of the invention to provide secondary lithium ion batteries which have high loadability, high energy output and/or high power and can be produced inexpensively for various crystal structures.

Surprisingly, it has been found that the specific charge of lithium intercalation compounds is high and the loadability of batteries produced therefrom can be improved if lithium oxide-containing lithium intercalation compounds having a particular morphology, namely in the form of agglomerates, are employed, where the agglomerates have a specific surface area, determined by the BET method, of from 0.1 to 3 m²/g, an agglomerate size, determined from the d₅₀ value, of greater than 6 μm, a diameter, determined from the d₉₀ value, of 100 μm or smaller, and intrapores having a size of from 0.3 μm to d₅₀/4, and an intrapore volume of at least 0.08 ml/g.

35 Thin-film electrodes of this type are produced by the
following general process, which is known per se:

In a vessel filled with the lithium intercalation compound according to the invention, graphite and conductive black, the pigments are mixed well. A solution of a generally customary electrode binder and
5 a solvent or solvent mixture in suitable amount is subsequently added to the pigment mixture and mixed intimately with the pigments. The resultant suspension is knife-coated or cast onto a thin aluminum foil. The solvent is subsequently removed at elevated
10 temperature. The coated foil is pressed between steel rolls and dried under reduced pressure until free from water. The moldings coated in this way can be employed as thin-film electrodes for the production of secondary lithium ion batteries.

15 It has furthermore been found that secondary lithium ion batteries which contain the lithium intercalation compounds according to the invention as active material of the positive electrode have high loadability at the
20 same time as high energy liberation or high performance and at the same time are inexpensive to produce.

Secondary lithium ion batteries of this type are produced in a manner known per se and essentially
25 consist of a positive electrode, a negative electrode, a separator and an electrolyte in a casing. For the secondary lithium ion batteries according to the invention, the lithium intercalation compounds according to the invention are used as active material
30 with a suitable binder known per se in the positive electrode, while the active material employed for the negative electrode is graphite or carbon or another host substance which is capable of taking up lithium ions, with a suitable binder known per se.

35 The lithium intercalation compounds according to the invention are distinguished by particularly good

processing and electrical properties and allow the combination of normally contradictory properties, for example the combination of a high specific surface area with a simultaneously high d_{50} value.

5

The specific surface area of the lithium intercalation compounds according to the invention, determined by the BET method, is in the range $0.1 - 3 \text{ m}^2/\text{g}$, preferably $0.3 - 1.5 \text{ m}^2/\text{g}$ and very preferably $0.5 - 1.2 \text{ m}^2/\text{g}$. The
10 agglomerate or particle size, measured from the d_{50} value, is greater than $6 \text{ }\mu\text{m}$, preferably greater than $10 \text{ }\mu\text{m}$. The diameter of the agglomerates, measured from the d_{90} value, is advantageously not greater than $d_{90} = 100 \text{ }\mu\text{m}$, preferably less than $d_{90} = 50 \text{ }\mu\text{m}$, very
15 preferably less than $40 \text{ }\mu\text{m}$. The particles have an agglomerate structure which has internal pores (intrapores) and external pores (interpores). The term intrapores here is taken to mean the pores in the interior of coherent agglomerates, while the term
20 interpores is taken to mean the pores which occur between the individual agglomerates and are dependent on the agglomerate size and shape, the particle size distribution and the resultant packing density.

25 The size of the intrapores d_{intra} depends on the agglomerate size d_{50} . Intrapores are always the same size as or smaller than a quarter of the agglomerate size d_{50} and are of equal size or larger than the surface roughness of the particles or agglomerates of
30 $0.3 \text{ }\mu\text{m}$. The following correlation thus arises for the size range of the intrapores:
size of the intrapores: $0.3 \text{ }\mu\text{m} \leq d_{\text{intra}} \leq d_{50}/4$.

The intrapore volume is the cumulative intrusion volume
35 in the size range of the intrapores. The lithium intercalation compounds according to the invention have an intrapore volume of at least 0.08 ml/g . The size of

the intrapores and the intrapore volume determine the performance and the preferred area of application of the lithium intercalation compounds according to the invention in secondary lithium ion batteries. Thus, 5 these lithium intercalation compounds are more suitable for the production of batteries in which high initial power and rapid energy liberation, i.e. high pulse loadability, is desired, the larger the intrapores and the intrapore volume. If, on the other hand, high 10 energy production is desired, relatively small values are selected for the intrapore size and intrapore volume.

The process according to the invention for the 15 preparation of lithium oxide-containing lithium intercalation compounds in agglomerate form consists at least of three steps:

I. preparation of a particulate precursor compound by 20 intimate mixing, heating and grinding of the starting materials,

II. preparation of a suspension of this particulate precursor compound in water with addition of a 25 polymeric binder, followed by spray-drying thereof, giving agglomerates, and

III. a heating step, in which the porous lithium intercalation compound according to the invention is 30 obtained.

The synthesis of a lithium manganese intercalation oxide having the morphology according to the invention by the process according to the invention is described 35 below as representative of various lithium oxide-containing lithium intercalation compounds:

1.1. Intimate mixing of the starting materials Li_2CO_3 and manganese oxide Mn_3O_4 . Suitable starting materials for the preparation of a lithium manganese intercalation oxide are also various other known
5 manganese and lithium compounds, for example Li_2O_2 , Mn_2O_3 or MnO_2 , or mixtures of lithium oxides or manganese oxides, so long as the mixture contains sufficient active oxygen. The preferred manganese compound is Mn_3O_4 and the preferred lithium compound is Li_2CO_3 . The active
10 oxygen promotes the linking of lithium to manganese during firing. The amount (number of equivalents) of active oxygen must be at least as large as the number of lithium atoms. Active oxygen can be introduced by the manganese compound so long as the manganese valency
15 is greater than 2. Each Mn valency greater than 2 supplies one equivalent of active oxygen, each Mn valency greater than 3 supplies two equivalents of active oxygen, etc. Active oxygen can also be introduced by the lithium compound, where each formal
20 Li valency greater than 1 (for example Li_2O_2) supplies one equivalent of active oxygen.

The mixing process generally takes between 10 and 60 minutes, but preferably from 15 to 45 minutes. Mixers
25 which can be employed here are all customary types of mixer, preferably mixers with integrated grinding tools.

1.2. Heating of the mixture, advantageously in a rotary
30 tube furnace, preferably under N_2 , argon, air, oxygen or an oxygen-containing gas at 600°C - 1000°C with a residence time of 15 - 120 minutes. The heating is preferably carried out under nitrogen at a temperature of from 700°C to 900°C and a residence time of 30 - 90
35 minutes.

1.3. Grinding of the heated mixture until a finely divided mixture is obtained. Suitable mills here are, for example, tin mills, impact disk mills, universal mills, jet mills or the like, optionally with
5 classification. It is also possible to carry out a plurality of grinding processes one after the other in identical or different mills.

The grinding is continued until the particle sizes of
10 the resultant particles have reached d_{90} values of smaller than 30 μm .

1.4. Optional additional step: re-heating as in point 1.2, where the temperature may be the same as or higher
15 than in point 1.2, but is not higher than 1000°C and is preferably not higher than 900°C. The residence time is likewise 15 - 120 minutes.

1.5. Optional additional step: re-grinding as in point
20 1.3, where the same or a different mill as in 1.3 can be selected and particle sizes and particle size distributions the same as or different from 1.3 are achieved.

25 2.1. Preparation of a suspension of the particulate precursor compound produced by working steps 1.1 to 1.3 or 1.1 to 1.5 in water with addition of an at least partially water-soluble, polymeric binder (where the term polymer is taken to mean at least a multiple, i.e.
30 at least a triple, of one or more monomers).

Suitable polymeric binders are polymers which form hydrogen bonds, such as cellulose, starch, gelatin, polyacrylates, polyvinyl alcohol and polyvinyl
35 acetates, in concentrations of from 0.1 to 5% by weight, based on the total weight of the solids employed. If less binder is employed, its binding

action is generally not sufficient to ensure the desired agglomerate formation to an adequate extent in the further working step. An amount of polymeric binder in excess of the stated range hardly increases the binding action at all, while increasing costs considerably, but may result in spontaneous combustion of the products at the high temperatures which prevail in the remainder of the process.

10 Polyvinyl alcohol in an amount of from 1 to 2% by weight is preferably added as polymeric binder.

The suspension can be prepared by generally known processes using known apparatuses, for example reactors or stirred tanks.

2.2 Drying of the suspension with formation of agglomerates of particulate precursor compound. The drying here is carried out as spray drying by means of processes and apparatuses which are known to be suitable for this purpose. It is preferred here for the spray drier to be operated at high speed with a two-component nozzle or an atomization disk. The drying is carried out at an exhaust-gas temperature of from 100 to 150°C, preferably from 105 to 120°C. The residual moisture content of the resultant dried agglomerates should not exceed 5%. The agglomerates should subsequently not be moistened or ground any further.

30 3. Heating of the dry agglomerates under an oxidizing atmosphere at 450-900°C at a residence time of from 0.5 to 10 hours.

In this step, the binder is generally burnt out without leaving a residue. The heating can be carried out in a rotary tube furnace, preferably at from 725°C to 900°C and - if the furnace is

5 fitted with a plurality of heating zones - at a reduced temperature of 450-750°C in the final heating zone. The residence time is preferably 0.5-6 hours. The oxidizing atmosphere is preferably generated using oxygen.

10 The heating can likewise be carried out in a stationary furnace under an oxidizing atmosphere at a preferred temperature of from 600°C to 750°C with a residence time of preferably greater than 5 hours. Here too, the oxidizing atmosphere is preferably generated using oxygen.

15 4. Optional additional step: suspension of the lithium manganese oxide intercalation compound in water with addition of one or more alkaline lithium salts, followed by spray-drying at temperatures of from 100°C to 400°C. Suitable alkaline aluminum salts are, for example, Li_2CO_3 ,
20 Li_2O_2 , LiNO_3 , LiOH or mixtures of two or more thereof. Preference is given to Li_2CO_3 . The spray-drying may be followed by post-drying at temperatures of from 100°C to 300°C in an oxygen-containing atmosphere, preferably in air.

25 In order to simplify the sintering, a sintering aid can be added in steps 1.1 to 2.2 in a concentration of from 0.1 to 3% by weight, based on the solids content. The sintering aid is preferably added during preparation of
30 the mixture, step 1.1, but alternatively during preparation of the suspension, step 2.1. The sintering aid employed is preferably a boron oxide, particularly preferably H_3BO_3 .

35 It is also possible to heat the agglomerates in step 3 initially under non-oxidizing conditions. However, this step must necessarily be followed by heating under an

oxidizing atmosphere as described in step 3. This procedure greatly increases the duration and costs of the preparation process and is therefore not preferred.

- 5 Thin-film electrodes which contain the agglomerated lithium oxide compounds prepared by the process according to the invention can be produced as follows:

10 The lithium oxide-containing lithium intercalation compound according to the invention, graphite and conductive black are weighed into a metal cylinder filled with steel balls. The cylinder is sealed and rolled on a rolling board, during which the pigments are mixed well. A solution of a generally customary
15 electrode binder, for example a fluorine-containing polymer having a fluorine content of greater than 50% by weight, and a suitable solvent or solvent mixture in suitable amount are subsequently added to the pigment mixture, and the cylinder is again rolled on the
20 rolling board until the maximum particle size has dropped below the range from 10 to 90 μm . The resultant suspension is cast onto a thin aluminum foil, and a wet-layer thickness of from 150 to 600 μm is established by means of a hand coater with adjustable
25 gap size. The solvent is subsequently removed, and the foil is heated at a temperature in the range from 80 to 150°C. In order to establish low porosity, the coated foil is pressed under pressure between steel rolls. The foil is subsequently split into parts of suitable size,
30 which are dried under reduced pressure until free from water.

In order to produce a secondary lithium ion battery, a thin-film electrode produced by the process described
35 above is used as cathode. The anode employed is a lithium electrode or a thin-film electrode consisting of graphite, carbon or another material which is

capable of taking up lithium ions, and a suitable binder. These electrodes are assembled together with a separator and an electrolyte and optionally further constituents in a casing to give a secondary battery
5 and charged. Secondary lithium ion batteries produced in this way have excellent service properties.

The lithium oxide intercalation compounds prepared by the process according to the invention have the
10 morphology described in claim 1 and can advantageously be used for the production of thin-film electrodes. The lithium oxide-containing lithium intercalation compounds according to the invention have an extremely positive effect on the service properties of secondary
15 lithium ion batteries which contain them as active material of the positive electrode. Thus, it is possible, for example, to predetermine the preferred suitability of the intercalation compounds for cells of high power or high energy liberation by adjusting the
20 intrapore volume to the requisite values, it being possible to ensure both high specific charge and high loadability of the cells.

A further advantage of the invention consists in that
25 the lithium intercalation compounds obtained can be prepared in the morphology according to the invention by the process according to the invention irrespective of the nature of the elements present other than lithium and oxygen, for example cobalt and/or nickel,
30 and irrespective of their crystal structure (spinel or layer structure) and have the advantages associated therewith.

The invention will be described in greater detail below
35 with reference to Figures 1 and 2 and a number of Examples, but is not restricted thereto.

Fig. 1 shows the relationship between the pore diameter and the cumulative pore intrusion volume for an Li/Mn spinel a according to Example 1

5

Fig. 2 shows the magnified electron photomicrograph of an Li/Mn spinel b according to Example 2.

Working Examples:

10

Example 1: Preparation of an Li/Mn spinel a

1.1 Mixing

15 712 kg of manganese oxide (Mn_3O_4 from Fermac, Ludwigshafen, after grinding in an Alpine 250 Z pin mill) and 184.5 kg of lithium carbonate (product ground to less than 40 μm from Chemetall, Frankfurt) were mixed for 30 minutes in a drum mixer with 3 knife heads
20 (capacity 2 m^3 , Lödige). The following measurement values were obtained from the mixture: bulk density: 0.7 g/ml, tamped density: 1.3 g/ml, specific surface area: 12 m^2/g .

25 1.2. and 1.3. Heating under N_2 and grinding

The mixture from 1.1 was heated in a gas-heated rotary tube furnace (Elino, length of heating zone 3.2 m, diameter 300 mm). The firing temperature was $750 \pm$
30 $10^\circ C$. 11 m^3 of nitrogen per hour were passed in co-current through the tube. The furnace atmosphere was protected against the ambient air by a double flap airlock valve at the tube end, so that the oxygen content in the rotary tube dropped below 1%. The
35 mixture was metered into the tube at about 30 - 40 kg/h. The tube rotated at 2 revolutions per minute. The inclination of the tube was 0.5 degree, so that the

residence time of the product in the heating zone was about 1 hour. A preliminary fraction of a few kilograms of product was discarded. 500 kg of fired product were subsequently collected. The product was ground in a pin mill (Alpine 250 Z). The following measurement values were obtained: bulk density: 0.8 g/ml, tamped density: 1.0 g/ml, specific surface area: 3 m²/g.

1.4 and 1.5. Heating under N₂ and grinding

The ground fired product from 1.3 was re-heated in the gas-heated rotary tube furnace (see above). The firing temperature was 825°C. 10 ± 1 m³/h of nitrogen were passed in co-current through the tube. The furnace atmosphere was protected against the ambient air by a double flap airlock valve at the tube end, so that the oxygen content in the rotary tube was less than 1%. The mixture was metered into the tube at about 25 kg/h. The tube rotated at 2 revolutions per minute. The inclination of the tube was 0.5 degree, so that the residence time of the product in the heating zone was about 1 hour. A preliminary fraction of a few kilograms of product was discarded. 169.5 kg of fired product were subsequently collected. The product was ground in a pin mill (Alpine 250 Z). The following measurement values were obtained: bulk density: 0.8 g/ml, tamped density: 1.4 g/ml, specific surface area: 1.1 m²/g.

1.5.1. Repetition of the grinding

Since the product from 1.5 still contained slightly scratching components, the grinding of a part quantity of 54 kg was repeated in a mill with classifier wheel (Alpine ZPS 50). The mill rotor speed was 15,000 rpm, and the classifier wheel rotated at 4000 rpm. The following measurement values of the classifier-ground product were obtained: bulk density: 1.0 g/ml, tamped

density: 1.3 g/ml, specific surface area: 1.4 m²/g. The particle size distribution was as follows: d₁₀ = 1.0 μm, d₅₀ = 3.0 μm, d₉₀ = 14 μm.

5 2.1. and 2.2. Preparation and drying of the suspension

A suspension of 2 kg of the classifier-ground product from 1.5.1, 4 liters of water and a solution of 20 g of polyvinyl alcohol (Mowiol 5-88, Hoechst) in 2 liters of
10 water (advantageously prepared in advance at the boiling point) was stirred in a beaker and dried for about 1.5 hours in a spray drier (Niro Minor) using an atomizer wheel. The atomizer gas pressure was about 4.8 bar. The heating-gas temperature was 350 ± 5°C, and
15 the exhaust-gas temperature was 110 ± 5°C. In this synthesis, 1.45 kg of pigment were isolated in the collecting vessel under the cyclone. The following measurement values were obtained: bulk density: 1.1 g/ml, tamped density: 1.3 g/ml, specific surface area:
20 1.5 m²/g.

3. Heating in an oxidizing atmosphere

The spray-dried powder from 2.2 was heated in an
25 electrically heated rotary tube furnace. The powder was metered into the tube at about 0.1 kg/h. The maximum heating temperature was 775°C (length of the heating zone 78 cm). 50 l/h of oxygen were passed through the tube (diameter 5 cm) in co-current. The tube rotated at
30 1/2 revolution per minute, so that the residence time of the product in the heating zone reached about 1 hour. The inclination of the tube was 5 degrees. A small part-amount (preliminary fraction) was discarded. 1.4 kg of fired product were collected. The following
35 measurement values were obtained:

Bulk density: 0.8 g/ml, tamped density: 1.1 g/ml, specific surface area: 0.7 m²/g, pH: 8.9, particle size distribution: d₁₀ = 10 μm, d₅₀ = 27 μm, d₉₀ = 44 μm.

5 The particle size distribution in the resultant lithium manganese spinel intercalation compound was determined using the mercury porosimetry method. Pores having a size of about 1 μm were clearly recognizable. The incremental intrusion volume at a pore size of 1 μm
10 reached a local maximum of 0.01 ml/g. Furthermore, pores (interpores) having a size of 10 μm were observed, which was evident from the fact that the incremental intrusion volume reached a local maximum of 0.07 ml/g at a pore size of 10 μm. The intrapore
15 volume, i.e. the cumulative intrusion volume in the size range of the intrapores of from 0.3 to 6.8 μm, of this spinel was 0.20 ml/g. The relationship between the cumulative intrusion volume and the pore diameter is shown in Figure 1.

20 The powder charging data were subsequently determined. A value of 109 Ah/kg of powder was found in the 5th discharge (lithium intercalation).

25 Example 2: Preparation of an Li/Mn spinel b

Steps 1.1 to 1.5.1 from Example 1 were repeated.

2.1. and 2.2. Preparation and drying of the suspension

30 A suspension of 4 kg of the classifier-ground product from 1.5.1, 3 liters of water and a solution of 60 g of polyvinyl alcohol (Mowiol 5-88, Hoechst) in 2 liters of water (advantageously prepared in advance at the
35 boiling point) was stirred in a beaker and dried for about 3 hours in a spray drier (Niro Minor) using a two-component nozzle. The heating-gas temperature was

240 \pm 20°C, and the exhaust-gas temperature was 150 \pm 3°C. The atomizer gas pressure was about 1.8 bar.

3. Heating in an oxidizing atmosphere

5

The spray-dried powder from 2.2 was heated in an electrically heated rotary tube furnace. The powder was metered into the tube at about 4.5 kg/h. The maximum heating temperature was 775°C (length of the heating zone 140 cm). 1.5 m³ of oxygen per hour were passed through the tube (diameter 25 cm) in co-current. The tube rotated at 4/3 revolutions per minute and paused for one minute every quarter revolution, so that the residence time of the product in the heating zone reached about 4 hours. The inclination of the tube was 0.25 degree. A small part-amount (preliminary fraction) was discarded. 6.9 kg of fired product were collected. The following measurement values were obtained: bulk density: 1.0 g/ml, tamped density: 1.3 g/ml, specific surface area: 0.9 m²/g, pH: 8.1, particle size distribution: d₁₀ = 6 μ m, d₅₀ = 15 μ m, d₉₀ = 28 μ m.

The powder charging data were subsequently determined. A value of 115 Ah/kg was determined for the 5th discharge of the powder.

4. Suspension and spray-drying with Li₂CO₃

A suspension of 2.95 kg of the fired product from 3., 2.95 liters of water and 29.5 g of lithium carbonate was stirred in a beaker using a Turrax dispersion unit and dried for 1 hour in a spray drier (Niro Minor) using a two-component nozzle. The heating-gas temperature was 350 \pm 10°C, and the exhaust-gas temperature was 108 \pm 4°C. The atomizer gas pressure was 2.2 bar. 2.2 kg of Li/Mn spinel having an Li₂CO₃ layer were obtained. The particle size distribution was

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as follows: $d_{10} = 5 \mu\text{m}$, $d_{50} = 12 \mu\text{m}$, $d_{90} = 24 \mu\text{m}$, specific surface area: $1.2 \text{ m}^2/\text{g}$. Finally, the powder was dried in air for 1 hour in a drying cabinet at 300°C .

5 Coherent, spherical, porous agglomerates having an approximate diameter of $10\text{-}20 \mu\text{m}$ were evident on a magnified electron photomicrograph (see Figure 2). The agglomerates appeared to be composed of primary particles having a diameter of $1\text{-}3 \mu\text{m}$ which were
10 partially sintered at the edges. Pores (intrapores) having an approximate size of $1 \mu\text{m}$ were readily visible in the interior of the spherical aggregates.

In addition, the pore size distribution was determined
15 using the mercury porosimetry method. An accumulation of pores having a size of $1.0 \pm 0.5 \mu\text{m}$ was clearly evident; the incremental intrusion volume reached a local maximum of 0.01 ml/g at a pore size of $1 \mu\text{m}$. Furthermore, pores (interpores) having a size of $4.5 \pm$
20 $1.5 \mu\text{m}$ were observed, which was evident from the fact that the incremental intrusion volume reached a local maximum of 0.048 ml/g at a pore size of $5 \mu\text{m}$. The cumulative intrusion volume in the range from 0.3 to $3 \mu\text{m}$ (intrapore volume) was 0.14 ml/g .

25

On determination of the powder charging data, a value of 107 Ah/kg was found in the 5th discharge.

The magnified electron photomicrograph of an Li/Mn
30 spinel prepared in this way is shown in Figure 2.

Example 3: Production of a pigment-coated thin-film electrode 1

35 The following pigments were weighed into a metal cylinder having a volume of 6 liters which was filled with 3 100 g of steel balls having a diameter of from 4

to 6 mm: 1 223 g of lithium manganese oxide (Li/Mn spinel) in accordance with Example 1 having a specific surface area of 0.7 m²/g, 72 g of conductive black having a specific surface area in the range from 40 to
5 400 m²/g, and 72 g of graphite. The metal cylinder was sealed, and the pigments were mixed well by rolling on the rolling board. 81 g of a copolymer of vinylidene fluoride and hexafluoropropylene in a solvent mixture comprising 980 g of tetrahydrofuran (THF) and 245 g of
10 N-methylpyrrolidone (NMP) were subsequently added. The mixture was rolled on the rolling board for 3.5 hours until the maximum particle size had reached 28 µm. The pigment suspension was sieved off from the steel balls. The suspension was subsequently cast onto an aluminum
15 foil having a thickness of 25 µm by means of a motor coater with adjustable gap size. After evaporation of the solvent, the coated foil was heated at 160°C for 2 hours and subsequently pressed between two steel rolls under a pressure of 6 bar. For the production of
20 test specimens, disks having a diameter of 36 mm were stamped out and dried overnight under reduced pressure until free from water. A coating weight of 275 g per square meter was found. The layer thickness was 115 µm, and the porosity was 34% by volume. The specific
25 resistance of the layer including the foil and the transition resistance was determined at 65 Ωcm.

The test specimens were tested in an electrochemical cell with lithium metal as countercathode. The
30 following electrochemical values were measured for the electrode according to Example 3 [Li dislocation (charging)/Li intercalation (discharging)]:
Capacity in 1st cycle: 112/104 mAh/g for the layer and 132/122 mAh/g for the spinel
35 Capacity in 10th cycle: 99/98 mAh/g for the layer and 117/115 mAh/g for the spinel
Loadability: 96.5%

Example 4: Production of a pigment-coated thin-film electrode 2

The following pigments were weighed into an apparatus as described in Example 3: 1 259 g of lithium manganese oxide (Li/Mn spinel) as in Example 2 having a specific surface area of 1.0 m²/g, 76 g of conductive black having a specific surface area of from 40 to 400 m²/g, and 76 g of graphite. After the pigments had been mixed, a solution of 86 g of a polymeric fluorine-containing binder having a fluorine content of 70% by weight in a solvent mixture comprising 769 g of tetrahydrofuran (THF) and 330 g of N-methylpyrrolidone (NMP) was added. The mixture was rolled on the rolling board for 2 hours until the maximum particle size had reached 14 µm. The pigment suspension was treated further as in Example 3 and subsequently cast onto an aluminum foil, heated and compressed. For the production of test specimens, disks having a diameter of 36 mm were stamped out and dried overnight under reduced pressure until free from water. A coating weight of 251 g per square meter was found. The layer thickness was 104 µm, and the porosity was 33% by volume. The specific resistance of the layer including the foil and the transition resistance was determined at 120 Ωcm. The test specimens were tested in an electrochemical cell with lithium metal as countercathode.

The following electrochemical values were measured for the electrode according to Example 4:

Capacity in 1st cycle: 120/95 mAh/g for the layer and 122/113 mAh/g for the spinel

Capacity in 10th cycle: 92/91 mAh/g for the layer and 109/108 mAh/g for the spinel

Loadability: 95.2%

Comparative Example:

1 147 g of a commercially available lithium manganese
oxide (Li/Mn spinel) having an intrapore volume of
5 0.04 ml/g in the intrapore size range from 0.3 to
6.8 μm and a volume from the roughness of the surface
(pores < 0.3 μm) of 0.04 ml/g, a specific surface area
of 1.2 m^2/g , 70 g of graphite as described in Example 3
and 70 g of conductive black as described in Example 3
10 were weighed into an apparatus as described in Example
3. The binder employed was a solution of 71 g of the
copolymer from Example 3 in a solvent mixture
comprising 890 g of THF and 222 g of NMP. The amounts
of binder and solvent were matched here to the enlarged
15 surface area of the spinel.

The apparatus was rolled on the rolling board until the
maximum particle size of 30 μm had been reached. The
coating and compression of the layer on the aluminum
20 foil were carried out as in Example 3. A coating weight
of 237 g/m^2 , a layer thickness of 101 μm , a porosity of
34% by volume and a specific resistance (including
aluminum foil and transition resistance) of 25 Ωcm were
determined.

25

Test specimens having a diameter of 36 mm were stamped
out of the electrode foil produced in this way and
tested in a cell with lithium metal as
counterelectrode.

30

The following electrochemical values were measured:
Capacity in 1st cycle: 116/107 mAh/g for the layer and
139/128 mAh/g for the spinel
Capacity in 10th cycle: 107/105 mAh/g for the layer and
127/126 mAh/g for the spinel

35

Loadability: 85.7%

Analytical studies:

1. Pore size distribution:

The pore size distribution in the pore size range between 0.01 and 100 μm was determined using the mercury porosimetry method with an Autopore II instrument (in accordance with DIN 66133). Using this method, intrapores, i.e. the pores within a coherent agglomerate, and interpores, i.e. the pores between different agglomerates, can be measured. Further pores (larger than 50 μm) arising from the loose bed of a powder and pores (smaller than about 0.3 μm) associated with the roughness of the surface, are also measured.

In addition, intrapores can be rendered visible with the aid of electron photomicrographs. Interpores are naturally dependent on the particle size, the particle size distribution and the shape. The interpore size is thus approximately one third of the particle size.

2. Specific surface area:

The specific surface area (BET) was determined using a Ströhlein Areameter from Ströhlein, Düsseldorf, by the one-point difference method of Haul and Dümbgen in accordance with DIN 66131. The pigments were dried at 140°C for at least 12 hours.

3. Particle size distribution:

The particle size distribution was determined by laser diffraction in a SYMPATEC HELOS instrument. In this measurement, a spatula tip of the powder to be analyzed was added to the circulating water bath (optical concentration: about 15 - 50%). The particles were distributed by ultrasound for 50 seconds before and during the measurement, which took 10 seconds. This

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measurement essentially determined the diameter of the coherent agglomerates.

4. Powder charge data:

5

The powder charge data were determined as follows:

10 Firstly, auxiliaries were mixed in a mill: 1 g of carbon black (for example Vulcan XC-72 or Ensaco 250) plus 1 g of graphite (SFG 10) plus 2.2 g of PVDF (Aldrich).

15 A coating comprising 2 g of spinel and 0.4 g of auxiliaries in NMP (N-methylpyrrolidone) was stirred using a high-speed stirrer. In order to produce the layer to be tested, the coating was sprayed onto the titanium collector, which had in each case been predried and slightly warmed, in up to four repetitions. The area of the current collector was
20 1.3 cm². Between each application, the coating was homogenized using the high-speed stirrer and immediately processed further in order to counter possible separation of the solids.

25 The coating was sprayed onto the prewarmed titanium collector with the aid of a spray gun (air brush spray gun) and dried. The most critical step for the reproducibility and correctness of the measurement was the weighing of the dried layer on the Ti collector.
30 The layer weighed about 25 mg; it was weighed to a resolution of 0.1 mg, corresponding to an error of 0.4%, in the case of differential weighing a maximum of 0.8%, but on average less.

35 The electrodes were dried for at least 12 hours at 120°C in an oil-pump vacuum before they were assembled into an electrochemical cell in a glove box filled with

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argon. The anode used was lithium metal (Aldrich, 99.9%, 0.75 mm thickness), and the commercially available electrolyte solution LP 30 (1M LiPF_6 in ethylene carbonate/dimethyl carbonate 1:1, Merck) was
5 furthermore used. The separator was a glass nonwoven with a thickness of about 2 mm. The geometry of the charge measurement cells is described in P. Novák, W. Scheifele, F. Joho, O. Haas, *J. Electrochem. Soc.* **142**, 2544 (1995), see there in particular Figure 1 (although
10 the reference electrode shown there was not used).

The charging and discharging were carried out in the potential range between 3.3 and 4.4 volts with constant currents of 10 μA per milligram of oxide, which
15 resulted in charging and discharging times in the order of greater than 10 hours in each case.

5. Foil charging data:

20 The foil charging data were determined as follows:

The aluminum pieces (diameter 36 mm) coated with lithium intercalation oxide were dried for at least 12 hours at 120°C under an oil-pump vacuum (pressure
25 about 10^{-2} mbar) in the lock of a glove box. They were subsequently processed further under a dry, oxygen-free argon atmosphere. An electrochemical cell was produced by assembling a stack of the coated aluminum disks, a separator disk (Celgard 2502, Hoechst) and a lithium
30 metal disk (Chemetall, 99%, thickness 0.25 mm), soaking the stack with commercially available LP 40 electrolyte solution (1 M LiPF_6 in ethylene carbonate/diethyl carbonate 1:1, Merck), and compressing the stack between two sealed-off steel plates under a pressure of
35 about 6 bar. The steel plate in contact with the coated aluminum foil was the plus pole, and the steel plate in contact with the lithium disk was the minus pole. The

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charging and discharging were carried out in the potential range from 3.3 to 4.3 volts with constant currents of about 40 μA per milligram of oxide, which resulted in charging and discharging times in the order
5 of greater than 2 hours in each case. The charging and discharging operations were repeated at least 10 times.

6. Loadability

10 The loadability of the cell was determined as follows: a charged cell (initial value 4.3 V) after the second charging was fast-discharged with three times the current, i.e. about 120 μA per milligram of oxide (corresponding to a load of about 3 mA/cm^2) to the final
15 discharge voltage of 3.3 V. The charge determined here was entered in the ratio for discharge with a 6-times smaller current (i.e. about 20 $\mu\text{A}/\text{mg}$ of oxide).

Loadability = (capacity with a load of 3
20 mA/cm^2) / (capacity with a load of 0.5 mA/cm^2) x 100 (%),
measured in the 2nd cycle.

7. Specific resistance:

25 The specific resistance of the layer was determined as follows: a circular piece of foil having an area of 10 cm^2 was compressed between two metal plates at 6 bar, and the volume resistance was measured after 10 seconds. The specific resistance is the same as the
30 volume resistance (unit Ω) divided by the layer thickness (unit cm) times 10 cm^2 .

8. Method for determining the intrapore volume

35 The intrapore volume was determined as follows: the pore size distribution in the pore size range from 0.01 to 100 nm was determined using the mercury porosimetry

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method with an Autopore II instrument (in accordance with DIN 66133). In addition, the d_{50} value of the particle size distribution was determined by laser diffraction. The intrapore volume is the pore volume
 5 integrated in the range from $0.3 \mu\text{m}$ to the value $d_{50}/4$ (μm).

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Patent claims

1. A lithium oxide-containing lithium intercalation compound for thin-film electrodes in the form of agglomerates, where the agglomerates have
 - a specific surface area, determined by the BET method, of from 0.1 to 3 m²/g,
 - an agglomerate size, determined from the d₅₀ value, of greater than 6 μm,
 - a diameter, determined from the d₉₀ value, of 100 μm or smaller and intrapores having a size of 0.3 μm ≤ d_{intra} ≤ d₅₀/4 μm, and an intrapore volume of at least 0.08 ml/g.
2. A lithium oxide-containing lithium intercalation compound as claimed in claim 1, where the specific BET surface area is from 0.3 to 1.5 m²/g.
3. A lithium oxide-containing lithium intercalation compound as claimed in claim 1, where the specific BET surface area is from 0.5 to 1.2 m²/g.
4. A lithium oxide-containing lithium intercalation compound as claimed in claims 1 to 3, where the agglomerate size, determined from the d₅₀ value, is greater than 10 μm.
5. A lithium oxide-containing lithium intercalation compound as claimed in claims 1 to 4, where the diameter, determined from the d₉₀ value, is smaller than 50 μm.
6. A lithium oxide-containing lithium intercalation compound as claimed in claims 1 to 4, where the diameter, determined from the d₉₀ value, is smaller than 40 μm.

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7. A lithium oxide-containing lithium intercalation compound as claimed in claim 1, where lithium manganese oxide is present.
- 5 8. A lithium oxide-containing lithium intercalation compound as claimed in claims 2 to 6, where lithium manganese oxide is present.
9. A process for the preparation of a lithium oxide-
10 containing lithium intercalation compound for thin-film electrodes in the form of agglomerates as claimed in claim 1, by
- a) preparation of an intimate mixture of one or
more lithium compounds and one or more
15 transition-metal compounds, followed by heating and grinding, giving a finely divided mixture;
- b) suspension of the finely divided mixture in
water with the addition of an at least
20 partially water-soluble polymeric binder, followed by spray-drying, giving agglomerates; and
- c) heating of the dry agglomerates in an
oxidizing atmosphere at from 450°C to 900°C.
- 25 10. A process for the preparation of lithium manganese oxide-containing lithium intercalation compounds for thin-film electrodes in the form of agglomerates as claimed in claim 1, by
- 30 a)
- a1) preparation of an intimate mixture of
one or more lithium compounds and one or
more manganese compounds, where at least
one of these compounds or the sum of all
35 compounds contains sufficient active oxygen that the number of equivalents of

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active oxygen is equal to or greater than the number of lithium atoms,

- 5 a2) heating of the mixture under nitrogen, argon, air, oxygen or an oxygen-containing gas at from 600 to 1000°C and a residence time of from 15 to 120 minutes in a rotary tube furnace,
- 10 a3) grinding of the heated mixture to give a finely divided mixture;
- 15 b) suspension of the finely divided mixture in water with addition of an at least partially water-soluble binder, followed by spray-drying, giving agglomerates;
- 20 c) heating of the dry agglomerates in an oxidizing atmosphere at from 450°C to 900°C and a residence time of from 0.5 to 10 hours.
- 25 11. A process as claimed in claim 10, where the heating in a2) and the grinding in a3) are carried out twice or more.
12. A process as claimed in claim 10 or 11, where the suspending in water is carried out with addition of polyvinyl alcohol as binder.
- 30 13. A process as claimed in claim 12, where polyvinyl alcohol is added in an amount of from 1 to 2% by weight, based on the total weight of the solids employed.
- 35 14. A process as claimed in any of claims 10 to 13, where the heating in an oxidizing atmosphere is carried out in a rotary tube furnace at a

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temperature of from 725°C to 900°C and a residence time of from 0.5 to 6 hours.

15. A process as claimed in any of claims 10 to 13,
5 where the heating in an oxidizing atmosphere is carried out in a stationary furnace at a temperature of from 600°C to 750°C and a residence time of greater than 5 hours.
- 10 16. A process as claimed in any of claims 10 to 13 and 14 or 15, where, after the heating in an oxidizing atmosphere, the resultant solid is suspended in water with addition of one or more alkaline lithium compounds, and the suspension is spray-
15 dried at a temperature of from 100°C to 400°C.
17. A process as claimed in claim 16, where the alkaline lithium compound is Li_2CO_3 , Li_2O_2 , LiNO_3 , LiOH or a mixture of two or more of these
20 compounds.
18. A process as claimed in any of claims 9 to 17, where the intimate mixing and/or the suspension is carried out with addition of a binder in the
25 presence of a sintering aid with a concentration of from 0.1 to 3%, based on the weight of the solids employed.
19. A process as claimed in claim 18, where the
30 sintering aid is a boron oxide.
20. A process as claimed in claim 19, where the sintering aid is H_3BO_3 .
- 35 21. A thin-film electrode for secondary lithium ion batteries, containing a lithium oxide-containing

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lithium intercalation compound as claimed in claim
1 as active material.

22. A thin-film electrode for secondary lithium ion
5 batteries, containing lithium manganese oxide as
claimed in claim 7 as active material.
23. A thin-film electrode for secondary lithium ion
batteries, containing lithium manganese oxide as
10 claimed in claim 8 as active material.
24. A secondary lithium ion battery containing a
lithium oxide-containing lithium intercalation
compound as claimed in claim 1 as active material
15 of the positive electrode.
25. A secondary lithium ion battery containing lithium
manganese oxide as claimed in claim 7 as active
material of the positive electrode.
20
26. A secondary lithium ion battery containing lithium
manganese oxide as claimed in claim 8 as active
material of the positive electrode.

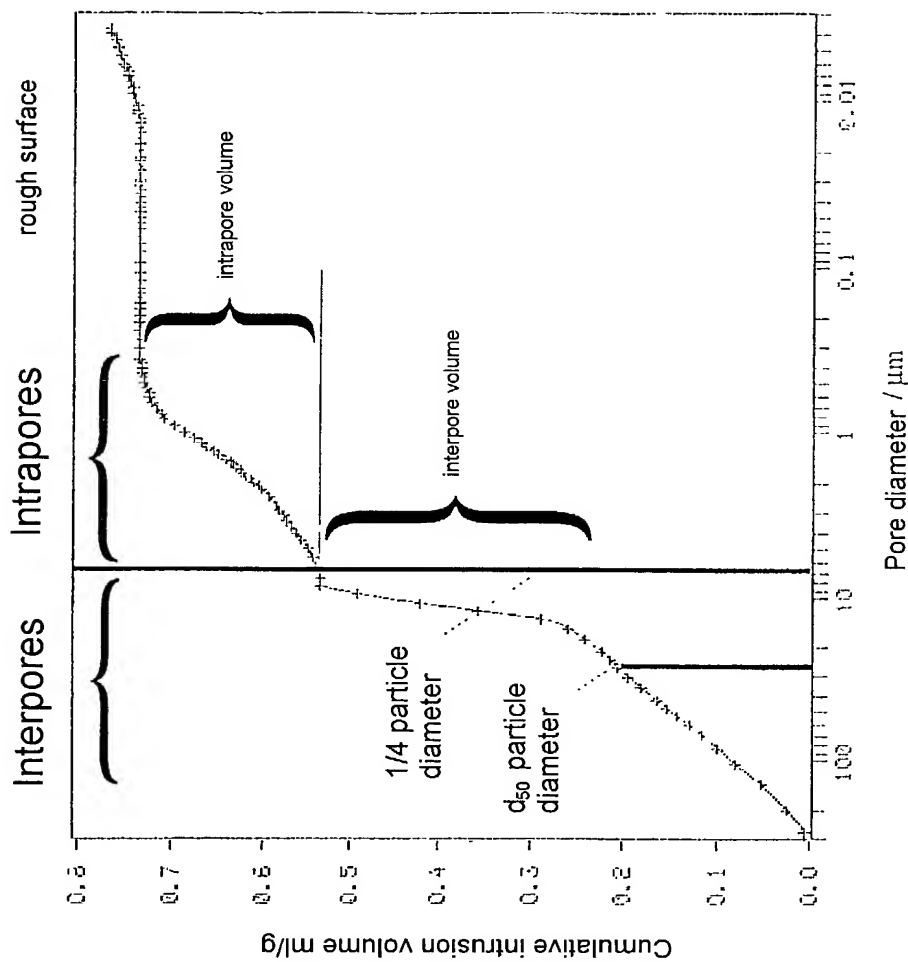
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Abstract

The invention relates to improved lithium oxide-containing lithium intercalation compounds having a particular morphology for thin-film electrodes, to a process for their preparation, to electrodes produced therefrom, and to secondary lithium ion batteries containing lithium oxide-containing lithium intercalation compounds as active material of the positive electrode which have high loadability, high energy release and/or high power and are inexpensive to produce.

Fig. 1



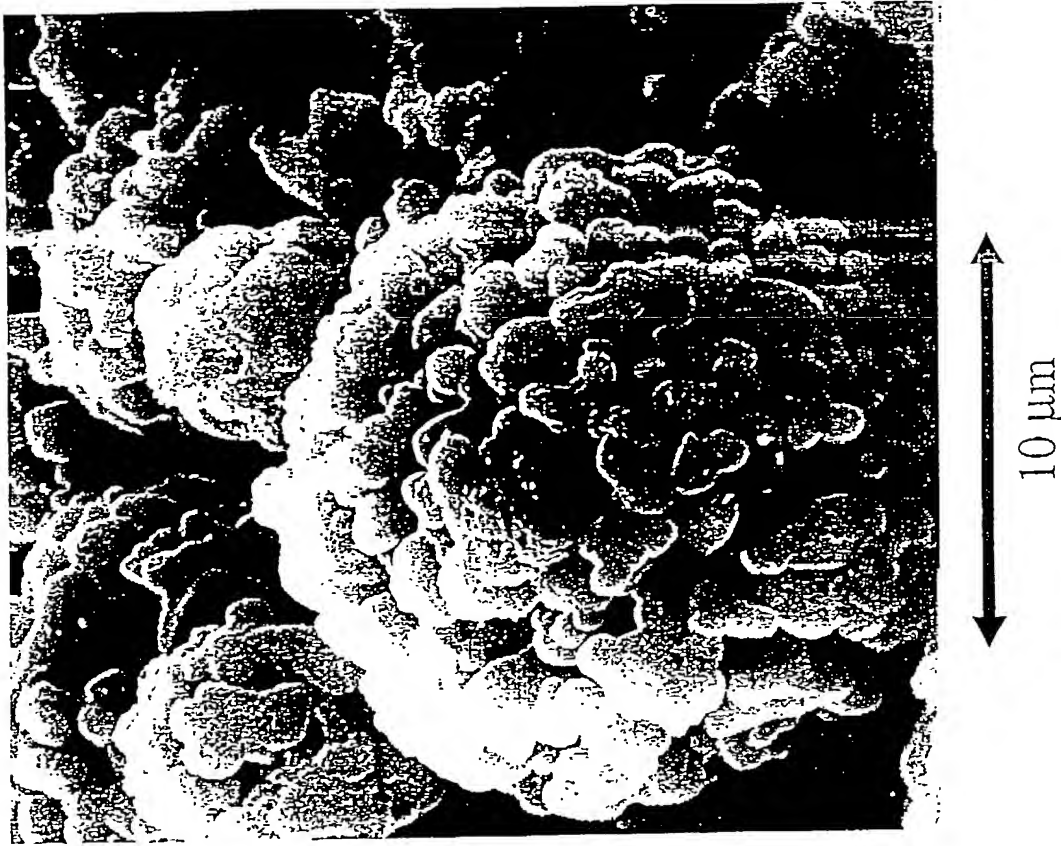


Fig.2

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Declaration and Power of Attorney For Utility or Design Patent Application

Erklärung für Patentanmeldungen zur Gebrauchseignung und Entwicklung.
mit Vollmacht

German Language Declaration

Als nachstehend benannter Erfinder erkläre ich hiermit an Eides Statt:

daß mein Wohnsitz, meine Postanschrift und meine Staatsangehörigkeit den im nachstehenden nach meinem Namen aufgeführten Angaben entsprechen, daß ich nach bestem Wissen der ursprüngliche, erste und alleinige Erfinder (falls nachstehend nur ein Name angegeben ist) oder ein ursprünglicher, erster und Miterfinder (falls nachstehend mehrere Namen aufgeführt sind) des Gegenstandes bin, für den dieser Antrag gestellt wird und für den ein Patent für die Erfindung mit folgendem Titel beantragt wird:

LITHIUMOXID ENTHALTENDE
LITHIUMINTERKALATIONSVERBINDUNGEN

deren Beschreibung hier beigelegt ist, es sei denn (in diesem Falle Zutreffendes bitte ankreuzen), diese Erfindung

☒ wurde angemeldet am 15 Juli 2000
unter der US-Anmeldenummer 10/031,932
und wurde am _____ abgeändert (falls zutreffend)
oder

unter der PCT internationalen Anwendungsnummer
PCT/EP00/06768 und wurde am _____ abgeändert
(falls zutreffend).

Ich bestätige hiermit, daß ich den Inhalt der oben angegebene Patentanmeldung, einschließlich der Ansprüche, die eventuell durch einen oben erwähnten Zusatzantrag abgeändert wurde, durchgesehen und verstanden habe.

Ich erkenne meine Pflicht zur Offenbarung jeglicher Informationen an, die zur Prüfung der Patentfähigkeit in Einklang mit Titel 37, Code of Federal Regulations, § 1.56 von Belang sind.

Ich beanspruche hiermit ausländische Prioritätsvorteile gemäß Title 35, US-Code, § 119 (a)-(d), bzw. § 365(b) aller unten aufgeführten Auslandsanmeldungen für Patente oder Erfinderurkunden, oder § 365(a) aller PCT internationalen Anmeldungen, welche wenigstens ein Land ausser den Vereinigten Staaten von Amerika benennen, und habe nachstehend durch ankreuzen sämtliche Auslandsanmeldungen für Patente bzw. Erfinderurkunden oder PCT internationale Anmeldungen angegeben, deren Anmeldetag dem der Anmeldung, für welche Priorität beansprucht wird, vorangeht.

Prior Foreign Applications

Frühere ausländische Anmeldungen

199 35 090.6

(Number)
(Nummer)

GERMANY

(Country)
(Land)

27 JULY 1999

(Day/Month/Year Filed)
(Tag/Monat/Jahr der Anmeldung)

(Number)
(Nummer)

(Country)
(Land)

(Day/Month/Year Filed)
(Tag/Monat/Jahr der Anmeldung)

☐ Zusätzliche einstweilige Anwendungsnummern sind im Prioritätsanhang aufgeführt.

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

LITHIUM OXIDE CONTAINING LITHIUM
INTERCALATION COMPOUNDS

the specification of which is attached hereto unless the following box is checked:

☒ was filed on July 15, 2000 as
United States Application Number 10/031,932
and was amended on _____ (if applicable)
or,

PCT International Application Number PCT/EP00/06768
and was amended on _____ (if
applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority under Title 35, United States Code §119 (a-d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT international application which designated at least one country other than the United States, listed below. I have also identified below, by checking the "No" box, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed:

Priority Claimed Prioritätsanspruch

<input checked="" type="checkbox"/>	<input type="checkbox"/>
Yes	No
Ja	Nein
<input type="checkbox"/>	<input type="checkbox"/>
Yes	No
Ja	Nein

☐ Additional foreign application numbers are listed on a supplemental priority sheet attached hereto.

German Language Utility or Design Patent Application Declaration

Ich beanspruche hiermit Prioritätsvorteile unter Title 35, US-Code, § 119(e) aller US-Hilfsanmeldungen wie unten aufgezählt.

(Application Number)
(Aktenzeichen)

(Application Number)
(Aktenzeichen)

(Application Number)
(Aktenzeichen)

- ☐ Zusätzliche einstweilige Anwendungsnummern sind im ergänzenden Prioritätsanhang aufgeführt.

Ich beanspruche hiermit die mir unter Title 35, US-Code, § 120 zustehenden Vorteile aller unten aufgeführten US-Patentanmeldungen bzw. § 365(c) aller PCT internationalen Anmeldungen, welche die Vereinigten Staaten von Amerika benennen, und erkenne, insofern der Gegenstand eines jeden früheren Anspruchs dieser Patentanmeldung nicht in einer US-Patentanmeldung, bzw. PCT internationalen Anmeldung in in einer gemäß dem ersten Absatz von Title 35, US-Code, § 112 vorgeschriebenen Art und Weise offenbart wurde, meine Pflicht zur Offenbarung jeglicher Informationen an, die zur Prüfung der Patentfähigkeit in Einklang mit Title 37, Code of Federal Regulations, § 1.56 von Belang sind und die im Zeitraum zwischen dem Anmeldetag der früheren Patentanmeldung und dem nationalen oder im Rahmen des Vertrags über die Zusammenarbeit auf dem Gebiet des Patentwesens (PCT) gültigen internationalen Anmeldetags bekannt geworden sind.

(Application No.)
(Aktenzeichen)

(Day/Month/Year Filed)
(Tag/Monat/Jahr eingereicht)

(Application No.)
(Aktenzeichen)

(Day/Month/Year Filed)
(Tag/Monat/Jahr eingereicht)

- ☐ Zusätzliche USA oder internationale Anwendungsnummern sind im ergänzenden Prioritätsanhang aufgeführt.

Ich erkläre hiermit, daß alle in der vorliegenden Erklärung von mir gemachte Angaben nach bestem Wissen und Gewissen der Wahrheit entsprechen, und ferner daß ich diese eidesstattliche Erklärung in Kenntnis dessen ablege, daß wissentlich und vorsätzlich falsche Angaben oder dergleichen gemäß § 1001, Title 18 des US-Code strafbar sind und mit Geldstrafe und/oder Gefängnis bestraft werden können und daß derartige wissentlich und vorsätzlich falsche Angaben die Rechtswirksamkeit der vorliegenden Patentanmeldung oder eines aufgrund deren erteilten Patenten gefährden können.

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I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below.

(Day/Month/Year Filed)
(Tag/Monat/Jahr der Anmeldung)

(Day/Month/Year Filed)
(Tag/Monat/Jahr der Anmeldung)

(Day/Month/Year Filed)
(Tag/Monat/Jahr der Anmeldung)

- ☐ Additional provisional application numbers are listed on a supplemental priority sheet attached hereto.

I hereby claim the benefit under Title 35, United States Code § 120 of any United States application(s), or § 365(c) of any PCT international application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of Title 35, United States Code § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

(Status)
(patentiert, schwebend, aufgegeben)
(patented, pending, abandoned)

(Status)
(patentiert, schwebend, aufgegeben)
(patented, pending, abandoned)

- ☐ Additional U.S. or international application numbers are listed on a supplemental priority sheet attached hereto.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

The undersigned hereby authorizes the U.S. attorney or agent named herein to accept and follow instructions from either his foreign patent agent or corporate representative, if any, as to any action to be taken in the Patent and Trademark Office regarding this application without direct communication between the U.S. attorney or agent and the undersigned. In the event of a change in the persons from whom instructions may be taken, the U.S. attorney or agent named herein will be so notified by the undersigned.

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VERTRETUNGSVOLLMACHT: Als benannter Erfinder beauftrage ich hiermit den sich mit der Kundennummer befassenden Patentanwalt (Patentanwälte) und/oder Patent-Agenten mit der Verfolgung der vorliegenden Patentanmeldung sowie mit der Abwicklung aller damit verbundenen Geschäfte vor dem Patent- und Warenzeichenamt und weise an, dass alle Korrespondenz mit dieser Kundennummer adressiert wird.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the attorney(s) and/or agent(s) associated with the Customer Number provided below to prosecute this application and transact all business in the Patent and Trademark Office connected therewith, and direct that all correspondence be addressed to that Customer Number:

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